

91

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90

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G L U T E N

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inclusive*

1. - The Composition of Wheat Flour Dough

1. Composition of flour. - Profound knowledge of the constitution of a natural colloid is, singularly, less advanced than that of an artificial colloid. The micella is the basic constituent of the latter. The micella remains the pivot of colloidal investigation the same as the atom is that of all classical chemistry. It is the result of the aggregation of composite granules of widely different origin; certain of these granules play an active part, others have a less important place and may have a more effective action, concealed, retarding or simply neutral.

It is difficult not to admit a certain similarity of structure between the natural and the artificial colloids; for the remainder, their physical properties are very much alike if not identical.

The micella is thus the basis of the intimate organization of natural colloids and more particularly of wheat flour.

As a matter of fact, can wheat flour be called a natural colloid? The question is an extremely delicate one.

Chemical analysis confirms the presence of the following substances which are the most characteristic among colloids:

Carbohydrates: starch, sugars, cellulose, fatty substances . . .

Proteins: particularly gliadine and glutinine which constitute the chief portion of which is called gluten.

Enzymatic substances: amylase, cytase, lipase, protease . . .

Hence, the micella of the flour appears to be a specific arrangement of the granules of the various compounds.

This structure is eminently unstable and very slight disturbances cause profound changes therein; it is an active entity, it is a center of incessant changes; it is a world of perpetual activity, wherein all the movements are regulated notwithstanding a most irregular aspect.

The configuration of a granule, as well as its internal structure, is essentially variable. Corresponding to these variations are those of the second degree in the colloidal properties of the aggregate, that is to say, the micella: The succession of reactions, the center of which is either within these particles or an assemblage thereof,

causes a succession of changes in the appearance of the granules and, hence, in that of the entire micella.

The flour grain should be considered as the result of a new agglomeration: as the granules produce the micella, so the latter produce the flour grain, which is sensitive to the touch by measured contact.

Intermicellar activity is comparable to intergranular activity and, through a result of the third degree, the reactions of the granule and the groups of granules modify the internal structure of the flour grain and its physical properties, thus its colloidal properties.

Those granules of greatest interest are:

the starch granule or grain and the protein granules or grains.

a) The starch grain. - Starch is of the following composition:

about 80% amylaceous substance,
about 20% water,
about 1% different substances: minerals,
nitrated . . . in the form of impurities.

The amylaceous substances are:

for about 80%, amylose
for about 20%, amylopectines with traces of
hemicellulose.

Wheat starch is present in the form of almost spherical isolated grains, visible to the microscope. Very thin superposed strata appear to issue from an eccentric hilum, giving the wheat starch grain a striated aspect like that of an onion, irregular and not sharply defined. The grain is a white mass slightly rough to the touch.

b) The protein grain. - Protein substances are present in very large number in wheat flour. Each has granules of special structure. The contacts vary in each substance; the successions are specific in each substance.

But they are assembled in the form of a kind of thread closely encompassing the starch grains. The two principal nitrated grains are located in the chains constituting the protein network;

The gliadine granule which is present in laminated form;

The glutinine granule, which is a pulverulent aggregate.

Like the starch grain, these protein grains contain widely diverse substances, such as minerals, fats, nitrates, etc.

2. Composition of the dough. - When the flour particles are in the presence of water certain changes are at once produced in this structure.

In the presence of a large excess of water the action of this new agent is of slight importance; each grain of flour is suspended in the water. These isolated grains are of no practical interest.

It is different when a limited quantity of water is incorporated. A specific hydrolysis of the insoluble corpuscles is produced. And the co-existence of all these related granules, attained simultaneously, brings about a very important change in the whole. This total change relates more particularly to the starch and protein grains.

The starch grain is immediately moistened superficially which gradually penetrates through the striations of the thin strata to the heart of the grain, carrying along certain soluble products and various organisms which tend to new activity in a new abode.

The insoluble protein grains react more completely: on the one hand, there is an inflation which gradually reaches the chains of the network constituting these substances; and, on the other, there is adsorption not only of the added water but of the dissolved materials, more particularly the numerous diastases contained in the flour. And it is this foreign vehicle which causes a progressive re-grouping of the protein constituents, producing a new configuration, always in the form of a thread, but also always in continuous change. The glutenine and gliadine granules form the more or less connecting elements which

produce the gluten.

Thus, in the micella, the center of incessant movements, the presence of water provides a new medium determining incessant changes and special groupings.

The dough particle may be considered as the development, about the slowly penetrated starch grain, of a protein chain, with constantly variable weft, and the constituents of which, inflated with water, retain the numerous substances which this latter provides or allows to enter.

This interlacing is imagined with difficulty, concerning which it is plausible to explain the cohesion and the movement through superficial forces which are exerted between the particles participating in the creation of a mass, the colloidal state of which is a gel.

It may be, however, possible to study profitably a limited case of the preceding where the dough, being completely freed from the starch grains, the gel assumes the simple order of united protein structures; this is the gluten.

II. - Production of Gluten.

1. Technique of Mr. Arpin. - A water is selected which tests about 20 to 25° hydrometric, temperature about 16°C, in a glass flask of 8 to 10 liters capacity, with two tubes, placed on a stand whereby the cock is about 35 centimeters above a table. Below the cock a white porcelain

dish, 30 centimeters in diameter, is covered with a screen lined with No. 60 metallic fabric.

33.33 gr. of the flour investigated are weighed out; 17 ccm. of water are poured on the flour placed in a brown enamelled porcelain mortar; mixing is done with a spatula and a homogeneous paste is obtained in two or three minutes of kneading; the paste obtained is then admixed between the fingers, it is softened, made homogeneous, so that it draws out well and does not adhere to the hands.

Mixing is then rapidly done under the cock of the glass flask, the water passing out in drops so rapidly that it is impossible to count them. The starch is eliminated under the pressure of the fingers. Separation should be effected in five minutes, and the gluten is washed for two minutes more.

Compression by hand or between two ebonite rollers produces in two minutes a compressed moist gluten; to obtain dry gluten it must be left in an oil stove for 12 hours at 105°C.

It is thus possible, by simple weighing, to determine the moist or dry gluten content of a flour; the difference is the hydration water of the gluten.

2. Description. - Kneading the flour and the water in a mortar produces a compact paste (dough) of the innumerable combinations precedingly described.

This dough is worked up under a stream of water, a method of obtaining gluten likewise known as lixiviation with water.

Lixiviation is a displacement method which consists in passing a continually renewed liquid through a substance containing soluble substances. Here, under the very slow action of the water, the starch grains are detached from the gel and flow off in a more or less whitish jelly. Participating in this escape are the soluble, mineral or nitrated materials, likewise the cellulosic waste and all impurities which the flour grains may carry.

Almost collaterally with these eliminations the diversely ramified groups of insoluble protein grains forms a gradually more coherent mass. This re-grouping is based on the reciprocal affinity of the gliadine and the glutenine grains. As a result of the disappearance of the starch grains, cellulosic debris . . . , the spaces between these granules is reduced; forces of cohesion increase at the points of contact; the gliadine lamellae become viscous, enveloping the glutinine grains, between which pass the mineral substances, fats, other nitrated substances; this mixture becomes more spongy, more agglutinant; the union becomes more intimate; and the ball which finally remains between the fingers is gluten.

A more or less elastic and extensible mass, gluten does not, properly speaking, exist in flour until the water produces the effects described, which are hastened and completed by the kneading.

Thus, wheat starch does not contain a constituent which could be called gluten. But the flour contains certain protein granules which when combined, through hydration, produces this gluten.

III. - Composition and Physical Properties of Gluten.

1. Composition of gluten. - It is necessary to distinguish gluten as obtained by the precedingly described technique from theoretical gluten which is practically unobtainable.

The former is called crude gluten, the second pure gluten. Pure gluten is a nitrated substance the weight of which is found from a knowledge of the nitrogen content of the crude gluten, with a slight deviation, since it is impossible that traces of nitrated substances will not remain incorporated in the cavities of the insoluble proteins.

The crude gluten of wheat flour contains about the following percentages of its two basic proteins:

60 to 82% of gliadine (which is a prolamine).

18 to 40% of glutenine (which is a gluteline).

Numerous tests showed that a good baking flour contains:

25% of glutenine for 75% of gliadine.

Noted by way of foreign elements and impurities are:

Cellulosic debris, starch grains, mineral substances, different nitrated and fatty materials . . .

Gliadine and glutenine are considered, in wheat flour, as the result of the addition or of the condensation of the following principal acid amines:

(The figures given on the table are merely indicative.)

	Gliadine	Glutenine
Glycocolle	---	0.89
Alanine	2.00	4.65
Valerianic acid	0.21	0.24
Leucine	5.61	5.95
Phenylalanine	2.35	1.97
Tyrosine	1.20	4.25
Serine	0.13	0.74
Cystine	0.45	0.02
Proline	7.06	4.23
Asparaginic acid	0.58	0.91
Glutaminic acid	37.33	28.42
Argenine	3.16	4.72
Lysine	---	1.92
Histidine	0.61	1.76
Ammonia	<u>5.11</u>	<u>4.01</u>
Total	65.80	64.68.

It is to be noted on first inspection of this table that complete knowledge of the acid amines constituting the two porteins is lacking. Numerous obscure points do not permit of certain deductions concerning the composition of

gliadine and glutenine.

It will be noted that gliadine contains neither glycocolle nor lysine. On the other hand, the glutaminic acid content is higher for gliadine than for glutenine.

Chemically, all the gliadines, as well as all the glutenines extracted from flours of widely different origin are shown to be almost absolutely identical. The differences found in the physical characters of glutens obtained with these flours must be attributed to the variable construction of the constituents of the spongy masses which these glutens form; thus, physical, that is to say colloidal, inequalities of the gliadine and glutenine grains in these flours.

Among the impurities found in crude gluten, an important place may be attributed to the fatty substances; their interposition between the different granules substantially modifies the physical cohesion and is an obstacle to the complete development of the attractive and, more particularly, the agglutinant actions of the protein network,

2. Physical Properties of Gluten. - 6.5 to 185% of gluten is extracted from a wheat flour after drying the moist gluten.

In the moist state gluten is a viscous substance, of variable hardness. Its elasticity is of all values, between that of short gluten which breaks easily, and ropy

gluten, which is almost impossible to break, its constituent fibers continuously expanding under traction.

Plastic, it generally returns to its initial mass and coalesces almost completely. However, certain hard glutens resist balling; the tissues have hard and dry profiles.

Others are more flexible and the reunion of a removed portion takes place very easily; the tissues are of lammellar form favoring re-incorporation; these lamellae sometimes contract slightly leaving cavities between the edges which roll up.

Almost odorless and tasteless, gluten nevertheless has an odor and a taste, although very slightly recognizable, greatly similar to that of freshly milled wheat flour.

Moist gluten dries rapidly when exposed to the air; the surface is strongly colored, becomes hard; the interior is interspersed with cavities of varying volume separated by fine membranes the texture of which resembles the crust of wheat bread.

Drying is facilitated by the oven. Hardening, rapidly produced, does not evacuate the internal moisture, which should be done subsequently. To effect this it is necessary to provide slits in the already formed crust.

The dry gluten thus obtained is extremely resistant to shock and its internal texture is as precedingly described.

Like in water, gluten is insoluble in ether, but partially soluble in alcohol, bases, dilute acetic and hydrochloric acids.

There is but little accurate information as to the elasticity and agglutinant and coagulant power of gluten.

IV. Panification and Gluten.

1. Generalities on Panification (Breadmaking).

Panary (bread) fermentation is the result of the combined actions of special agents existing either in the flour or in the yeast introduced in the dough.

In the first place, it consists of an action of the carbohydrates. More particularly, it is a hydrolysis of the starch grains which terminates in a production of glucose. The bacteria of the yeast act on this glucose and other sugars of various origin. Alcoholic fermentation then occurs: after a complex cycle of oxidations and multiple reactions caused by a diastase group, alcohol, carbon dioxid, traces of glycerin and its derivatives . . . are formed.

Certain authors acknowledge that this hydrolysis of the starch, which follows the alcoholic fermentation, is accompanied with the conversion of the insoluble nitrated substances in the following manner: through the action of a proteolytic ferment the gluten becomes insoluble, is hydrated and produces peptone; a bacilla assimilates this peptone furnishing numerous excretion products, among which: carbon dioxid, hydrogen, nitrogen, alcohol, acetic, butyric and lactic acids, leucine, tyrocine and phenol.

Before this conversion an inflation takes place through the action of the carbon dioxid produced in the alcoholic fermentation; the threads of the nitrated substances, as previously stated, absorb water to form an elastic gel similar to although less homogeneous than that obtained under the name of gluten; the tenacity of this gel decreases gradually in proportion as the quantity of water increases; and when the carbonic anhydride has become sufficiently abundant, occlusion thereof in the protein cells at the flexible walls causes the inflation.

The entire mass swells (rises), cavities are formed, deformed and sometimes open up to be emptied: the dough has risen. At the end of a certain time, after a number of mechanical operations, it is placed in the oven.

The proteins resulting from the action of the nitrated materials are coagulated by the heat of the oven into

a complex coating of other substances constituting the bread. Caramelization of the dough takes place which produces the protective crust. Under this crust the doughy mass continues its transformations as long as the temperature permits the bacteria and diastase to act. The water is finally evaporated, and the soft part of the bread is formed, having large and numerous cavities varying according to the baking operation: small cavities when the direct use of yeast, large cavities when leavening dough is used.

2. Two Important Factors. - Among the principal factors of the fermentation it is necessary to distinguish: the quantity of proteins and the "medium". The first is, of course, a function of the value of the flour used. The quality of the dough depends on the number of corpuscles forming the protein chains or nets. The partial deficiency of nitrated grains is, above all, the indication of a poor flour.

The second, properly speaking, is a result; and all the materials entering into the manufacture of bread contribute to give the "medium" all its chemical importance. It is this factor for which physical chemistry suggests the synthetic term: hydrogen ion or pH concentration, Soerensen.

The enzymatic and proteolytic activities depend on the medium in which they are called on to act. If it is admitted that an ideal succession of multiple

panification reactions takes place, it may be that, in a specific case, there is a greater or less departure from this ideal succession, as a result of disturbances of the medium. It is thus logical to attribute to a modification of the medium modification in the structure and the cohesion of the nitrated corpuscles, said structure and cohesion being elements of the quality of the dough.

It is generally admitted that the optimum value of the pH of panary fermentation is pH=5. This is likewise the value attributed at the isoelectric point of the gluten.

The number of nitrated grains, that is to say the protein quantity factor, is almost impossible for the investigator to rectify; it is essentially such as nature provides it in the constitution of the wheat grain endosperm.

The medium factor, on the contrary, is capable of being modified to a certain degree, particularly by the addition of acids. It is hence possible to act on the diastasic reactions and thus on the structure and bonds of the grains. These two elements - structure and bonds - determining the quality of the protein materials, the baker possesses a not unimportant means of modifying this quality, by improving the physical properties of the gluten, mainly increasing its elasticity, which increases its expansive force through the action of carbon dioxide, particularly in the oven.

V. - Applications.

The preceding theory permits of explaining some aspects of present technique, the most characteristic of which are:

1. Round and flat flours. - It is unanimously recognized that, among the whole wheat flours (this flour is obtained by reducing the entire grain of wheat), a round flour acts very much better during panification than a flat flour.

A flour is called round, the grains of which have a discontinuous granulose form, offering surfaces hard to measured contact, like those of a very fine sand.

Flat flour, on the contrary, is that recognized by a soft touch, like that exerted on an amorphous powder; it forms platelets under very light pressure, even of slight thickness. A flat flour may be obtained in two principal ways:

a) By poor milling of sound wheat - the most frequent case - when passed between through millstones too close together or tight cylinders gives heated and strongly crushed unbolted flour. The flour grain is altered, not by the heating of the material, which in most cases is below the limit in which the nitrated materials is modified by the heat, but simply by mechanical action of the too great flattening which destroys the constituent grains.

b) By milling a wheat having a poor or damaged internal structure. The unbolted flour resulting is properly prepared but the primitive structure, having been vitiated of the endosperm, furnishes only a badly organized, a "dead" flour.

Through one or the other of these methods, or through premeditated or accidental combinations of these two kinds of milling, only a poor quality of breadmaking flour is produced; the various protein chains, particularly, undergo a treatment contrary to the normal development of their activities.

Round flours, made from properly ground sound wheat, have the same chemical composition as flat flours; but the physical structure of the former is such that they are the only ones which can undergo the desirable conversions of the gel constituted by the dough obtained from these flours inasmuch^{as}/, more specifically, they are the only ones which permit of the normal reciprocal actions of the protein grains which are the source of their evolution. (The same explanation may be given to justify the relative values of the numerous varieties of flour obtained during the course of milling. Each passage: grinding, drying, ageing, converting . . . furnishes a flat or round flour. Although extracted from the same wheat these flours differ, either because of the difference in the internal structure of the grain, or the treatment of the products from which they are

formed. A modern mill furnishes twenty-five flours, the admixture of which is whole wheat flour).

2. Panification of Rye. - Rye flour is widely used in certain countries. It has also been used as a substitute for wheat flour during recent years.

Its panification is not as successful as that of wheat flour. The preceding explanation relative to the differences found between round and flat flours is sufficient therefor.

Quantitatively, rye flour, among other constituents, contains:

Glutenine	91.83
Gliadine	8.17
	<u>100.00</u>

average figures.

But qualitatively the nitrated grains are physically inferior to those of wheat flour. The gluten of a rye flour is not assembled (collected); the precedingly described kneading method fails. As a result a rye flour dough contains a protein network less cohesive than that of a wheat flour dough.

Rye bread rises poorly; it is flatter and more compact than wheat bread; the internal structure of the rye flour grain, by reason of the inferiority of its protein threads, is not so good as that of wheat flour for the various panification operations.

The function performed by incorporating a quantity, however small, of rye flour in wheat flour is very significant; panification is poor as compared with that of wheat flour, but rye flour causes a disturbance in the panification of wheat flour. The rye protein grains, endeavoring to participate in the erection of a common protein edifice with the wheat protein grains, produce non-coherent structures, very much decreased in vigor and hence incapable of furnishing fermentation results comparable with those which can be attained with that of a pure wheat flour.

The production of gluten from a wheat flour to which rye flour has been added is particularly difficult. There is a loss, not only of quality, but also of weight which exceeds that which might be expected from the percentage of rye flour incorporated. There is a sharp lack of harmony between the granules constituting the two nitrated networks.

This last observation is the most remarkable justification of the theory of the non-preexistence of gluten in flours.

3. Possible Improvements of the Two Chief Factors of Panification. - The study of panification has led to the recognition, among the factors of transformations through which it takes place under the action of the bacteria introduced with the yeast, or the fermentation proper of the dough:

a) the quantity of proteins

b) the medium.

a) The protein quantity factor. - It is almost completely neglected by the baker. Nevertheless, it is current milling practice to add bean flour to wheat flour. This flour is recognizable by its two physical properties: odor and color. Its odor, very strong, is likewise very disagreeable. Its appearance varies according to the origin of the grain; it is generally of a greenish yellow color. The beans employed are of domestic and foreign origin; they are cultivated to a small extent in France, the English Channel region, Oraine; large quantities are exported from China, Tunis, Asiatic Turkey.

The incorporation of up to 4% of bean flour is authorized. Its principal advantage lies in its high content of nitrogenous substances; as a matter of fact, bean flour contains a high percentage of glutenine. Its average content is

8 of gliadine for
92 of glutenine.

Certain wheats are deficient in glutenine. This is rectified by the incorporation of the nitrated materials of bean flour, the granules of which unite with those of the wheat to form a coherent network.

This modification of the total content of proteins of flour subjected to fermentation has been known for many

years. However, it is not as great as might be imagined. The strong odor of the bean flour impregnates and even overcomes that of the wheat flour. Its color is likewise an obstacle to a greater addition. In general, not more than 2% should be added.

2. The medium factor. - This factor may be modified, and Anglo-Saxon bakers chiefly practice various methods therefor.

It has been noted that the addition of a certain quantity of acids, either directly: hydrochloric, phosphoric, acetic, lactic acids; or indirectly: phosphates, aluminum sulfate and chloride, Humphrit salts, to the water of the dough, produces better panification. The most favorable results are obtained when the pH of the medium is about 5. On the basis of this laboratory confirmation, the previous methods appear plausible.

The function of these substances, called ameliorants, is to modify the acidity of the medium so that the pH will attain the optimum value; and this value corresponds to that, wherein the proteolysis is the most complete.

With this same means it is possible, in certain regions, to correct too strongly basic water, which permits of but mediocre panification.

Here also the importance of these methods is not exaggerated. They demand experience together with great ability. And the remark of an eminent Canadian cerealist shows the difficulty of panification experts: "I can not believe but that fortune awaits the baker who will have the courage to provide the public with perfectly baked bread, made with otherwise simple materials and having all the good flavor of home baked bread. Such bread, no doubt, will not please everybody, but will surely be preferred by thousands of people!"

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